

case of these two metals. In this connection it is interesting to notice that the effect of hydrogen on the constant  $\alpha_0$  for the positive emission from platinum is opposite to that for the negative emission for this metal, and is in the same sense as that for the negative emission from tungsten. These differences are to be expected if it is a question of the sign of dissolved or adsorbed ions.

In concluding, the writer ventures to hope that the considerations which have been brought forward will help to introduce some degree of orderliness into the experimental values of the emission constants, which, it must be admitted, are at present somewhat incoherent.

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*General Equations for the Neutralisation of Dibasic Acids, and their Use to Calculate the Acidity of Dilute Carbonate Solutions.*

By E. B. R. PRIDEAUX.

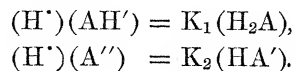
(Communicated by Prof. F. G. Donnan, F.R.S. Received May 26, 1915.)

The numerous equations which have been proposed to express the equilibrium of acids, bases, salts, and their ions are generally convenient to apply, since in each particular case different simplifying assumptions can be made. The subject has now reached a stage, however, at which these can be replaced by equations of a more general nature.

Practically the most important cases are those of the mono- and poly-basic acids combined with strong monacid bases, which furnish the bulk of those mixtures of balanced hydron concentration which are used in physiological chemistry and also effect the physical regulation of the physiological fluids themselves.

The relation between the stage of neutralisation and the hydron concentration of these acids is such that, usually, only two dissociation constants need to be considered. Thus the constants of a tribasic acid, such as orthophosphoric, are each one of a higher order of magnitude than that which precedes it, and at the stage of neutralisation at which the third constant begins to have an effect, that of the first is inappreciable. The general equation for a weak dibasic acid will alone be considered in what follows.

This will dissociate in the steps—



The degrees of dissociation  $\alpha_1$  and  $\alpha_2$  may be defined as the ratio of the primary (HA') and secondary (A'') ion respectively, to the total acid in any form of combination, *i.e.* as ions, undissociated acid and undissociated salt. Hence (HA') =  $\alpha_1 C$ , (A'') =  $\alpha_2 C$ .

In the simplest possible case, the total concentration is such that the dissociation of all salts may be taken as unity. If at the same time the concentration is not so low that the production of the hydrion and hydroxyl-ion necessary for the equilibria causes a rearrangement of a considerable fraction of the salt present; then it has been shown by Michaelis\* that—

$$\alpha_1 = \frac{K_1(H')}{(H')^2 + K_1(H') + K_1K_2},$$

$$\alpha_2 = \frac{K_1K_2}{(H')^2 + K_1(H') + K_1K_2}.$$

If the total acid concentration is C, then the ionised part is  $\alpha_1 C$ , etc., and the number of equivalents of ionised acid are equal to the added base.

Hence 
$$\frac{\text{equivalents base}}{\text{mols. acid}} = R = \frac{A' + 2A''}{C} = \alpha_1 + 2\alpha_2.$$

And the expression above may be transformed into

$$R = \frac{1}{1 + K_2/(H') + (H')/K_1} + \frac{2}{1 + (H')/K_2 + (H')^2/K_1K_2}. \quad (1)$$

This formula does not give quite accurate results when the total concentration is high, and especially at high alkalinities. It fails altogether at very low concentrations.

In order to include these cases also, an extension may be made of the method applied by the author to the correction of the third dissociation constant of orthophosphoric acid.

The ratio (R) of equivalents alkali to mols. of acid is equal to

$$\frac{(\text{NaHA}) + 2(\text{Na}_2\text{A}) + (\text{NaOH})}{(\text{NaHA}) + (\text{Na}_2\text{A}) + (\text{H}_2\text{A})}. \quad (2)$$

Also  $\text{NaHA} = (HA')/\alpha_1$ ,  $(\text{Na}_2\text{A}) = (A'')/\alpha_2$ ,

$$(\text{NaOH}) = \frac{(OH')}{\alpha_3} = \frac{K_w}{(H')\alpha_3},$$

in which  $\alpha_1$ ,  $\alpha_2$  now stand for the fractions dissociated, not of the total acid, but of the primary and secondary salt.

By the help of these, and of the ionic equations

$$(H')(HA') = K_1(H_2A), \quad (H')(A'') = K_2(HA'),$$

\* 'Die Wasserstoffionen Konzentration,' p. 30.

all the terms of equation (1) above, except the third term of the numerator, may be transformed into terms containing either (NaHA) alone or (Na<sub>2</sub>A) alone.

By the first method

$$R = \frac{(\text{NaHA}) + 2K_2(\text{NaHA}) \alpha_1 / (\text{H}^+) \alpha_2 + K_w / (\text{H}^+) \alpha_3}{(\text{NaHA}) + K_2(\text{NaHA}) \alpha_1 / (\text{H}^+) \alpha_2 + (\text{H}^+) (\text{NaHA}) \alpha_1 / K_1}. \quad (2a)$$

By the second method

$$R = \frac{2(\text{Na}_2\text{A}) + (\text{H}^+) (\text{Na}_2\text{A}) \alpha_2 / K_2 \alpha_1 + K_w / (\text{H}^+) \alpha_3}{(\text{Na}_2\text{A}) + (\text{H}^+) (\text{Na}_2\text{A}) \alpha_2 / K_2 \alpha_1 + (\text{H}^+)^2 (\text{Na}_2\text{A}) \alpha_2 / K_1 K_2}. \quad (2b)$$

Or dividing through by (NaHA), etc.,

$$R = \frac{1 + 2K_2 \alpha_1 / (\text{H}^+) \alpha_2 + K_w / (\text{H}^+) (\text{NaHA}) \alpha_3}{1 + K_2 \alpha_1 / (\text{H}^+) \alpha_2 + (\text{H}^+) \alpha_1 / K_1}, \quad (3a)$$

$$\text{or} \quad R = \frac{2 + (\text{H}^+) \alpha_2 / K_2 \alpha_1 + K_w / (\text{H}^+) (\text{Na}_2\text{A}) \alpha_3}{1 + (\text{H}^+) \alpha_2 / K_2 \alpha_1 + (\text{H}^+)^2 \alpha_2 / K_1 K_2}. \quad (3b)$$

If the third terms of the numerators are omitted, and the simplifying assumptions of p. 536 are introduced, it may easily be shown that either of these equations becomes identical with the transformed Michaelis' equation (1).

If the equations 3a and 3b are used as they stand, the former is suitable for solutions containing only small proportions of alkali, the latter for solutions containing small proportions of acid. The two give identical results for solutions containing moderate proportions both of HA' and of A''.

If the total concentration is moderate, (NaHA) and (Na<sub>2</sub>A) in the third terms may be obtained with sufficient accuracy from the amounts of acid and alkali taken.

*Dilute Solutions.*—At higher dilutions, the hydrolysis appreciably affects the amounts of primary and secondary salt. The third terms of the numerators must then be expressed differently.

Let C, as before, be the total concentration of H<sub>2</sub>A and its ions.

Then either A'' or H<sub>2</sub>A will be vanishingly small in comparison to the other two forms of combination.

Which form may be neglected is easily to be determined by means of the K<sub>1</sub> and K<sub>2</sub> equations on p. 536 combined with the value of (H<sup>+</sup>) chosen.

In the more acid solutions

$$C = (\text{HA}') + (\text{H}_2\text{A}).$$

And, since ionisation is practically complete,

$$(\text{NaHA}) = (\text{HA}').$$

Or, substituting for  $H_2A$  its value  $\frac{(H')(HA')}{K_1}$ , it follows that

$$(HA') = (NaHA) = \frac{K_1 C}{K_1 + (H')}.$$

Similarly, it may be shown that in the more alkaline solutions

$$(A'') = (Na_2A) = \frac{K_2 C}{K_2 + (H')}.$$

The complete equations for high dilutions become

$$R = \frac{1 + 2 K_2 / (H') + K_w \{K_1 + (H')\} / (H') K_1 C}{1 + K_2 / (H') + (H') / K_1}, \quad (4a)$$

and 
$$R = \frac{2 + (H') / K_2 + K_w \{K_2 + (H')\} / (H') K_2 C}{1 + (H') / K_2 + (H')^2 / K_1 K_2}. \quad (4b)$$

These equations are the quantitative expression of the fact that extreme dilution increases the amount of alkali required to produce a given value of  $(OH')$ . The third term of the numerator is a measure of the extent to which the hydron concentration of a given partly neutralised acid varies with the dilution.

*Application to Carbonic Acid.*—The carbonate equilibrium is the chief physical agent which regulates the hydron concentration, not only of physiological fluids, but also of the hard waters, fresh and salt, the acidity of which has so intimate a connection with the growth of plankton and other simple organisms. This acidity may in most cases be directly determined, but the determination is sometimes inconvenient.

In an important research, *e.g.* by Bronsted and Lund\* on the physical and biological conditions of Danish lakes, the amount of  $CO_2$  and of  $CaO$  has been determined in each case, but not the acidity of the water. The use of the equations will, it is hoped, enable the missing datum to be supplied in cases such as these.

The acidities of carbonic acid at different stages of neutralisation as determined by Auerbach and Pick† and others, may now be compared with those calculated by the different formulæ given above, using  $K_1 = 3.04 \times 10^{-7}$ , Walker and Cormack, and  $K_2 = 6 \times 10^{-11}$ , Shields, Koelichen, McCoy, Auerbach and Pick (*loc. cit.*).

Experimental Values at  $C = 0.2$  mol.  $H_2CO_3$  per litre.

R	=	1.00	1.05	1.10	1.20	1.30	1.40	1.50	1.60
$-\log(H')$	=	8.35	8.90	9.15	9.45	9.65	9.96	10.10	10.35
R	=	1.70	1.80	1.90	2.00				
$-\log(H')$	=	10.45	10.65	11.00	11.59				

\* 'Chem. Phys. Untersuchungen der Dänischen Gewässer,' 1912.

† 'Arb. aus d. Kais. Gesundheitsamt,' vol. 38, (4), p. 562 (1912).

The first Table given below has been calculated from formulæ 3*a* and 3*b*, p. 537, using  $\alpha_1 = \alpha_2 = 0.8$  and  $\alpha_3 = 0.9$  in a 0.1 molar solution. The second Table is from the simplified formula 1, p. 536. The two give almost identical results in the middle of the neutralisation curve at  $(H') = 1 \times 10^{-10}$ . But in the more alkaline solutions the introduction of the third term makes a considerable difference.

Thus by interpolation on the curves,  $-\log(H') = 11.7$  from the general formula, and 12.3 from the simplified formula at  $R = 2$ . The former thus gives a better agreement with the experimental values of Auerbach (11.4 at  $(Na_2CO_3) = 0.05$ ) than the latter.

Table I.

$-\log(H') = (3.75)$	5.00	6.00	6.70	7.00	7.30	8.00	9.00
R = (0.0)	0.037	0.27	0.66	0.79	0.89	0.96	1.05
$-\log(H') = 9.50$	10.00	11.00	11.50	12.00	12.30		
R = 1.16	1.375	1.86	1.97	2.05 <sub>5</sub>	2.13 <sub>5</sub>		

Table II.

$-\log(H') = 3.75$	5.00	6.00	6.70	7.00	10.00	11.00	12.00	12.3
R = 0.00	0.03	0.24	0.60	0.75	1.375	1.86	1.98	1.99

*Dilute Carbonate Solutions.*—The calculation of the acidity of solutions, of which the total concentrations are lower than those of  $CaCO_3$ , etc., in presence of the specified amounts of  $H_2CO_3$ , are, of course, equally applicable to carbonates of the calcium group as to those of the sodium group. There are a few experimental values of the  $(H')$  of hard waters which will serve to check the accuracy of the values in Tables III and IV, which are based on equations 4*a* and 4*b*.

Table III.

$C = 0.001$  mol.  $H_2CO_3$  per litre.

$-\log(H') = (4.75)$	5.00	6.00	6.70	7.00	8.00	9.00	10.00
R = (0.00)	0.03	0.23	0.60	0.75	0.975	1.06	1.44
$-\log(H') = 10.50$	11.00						
R = 1.86	2.50						

Table IV.

$C = 0.0001$ .

$-\log(H') = 5.26$	5.50	6.00	6.70	7.00	8.00	9.00	10.00	10.50
R = 0.00	0.09	0.23	0.60	0.76	0.98	1.12	2.01	3.62

In a 0.001 molar solution of  $Na_2CO_3$  Auerbach (*loc. cit.*) found

$$(OH') = 0.27 \times 10^{-3} \quad \therefore (H') = 2.37 \times 10^{-11}, \quad -\log(H') = 10.63.$$

The solubility of  $CaCO_3$  (calcite) is, according to Schloesing\* and Kohlrausch

\* 'Comptes Rendus,' vols. 74, 75 and 90 (1872 and 1880).

and Rose,\* 0.13 mgrm. mols. per litre. McCoy and Smith estimate it as 0.166, and Kendal† as 0.1433 at 25°. McCoy and Smith‡ state that the alkalinity of this solution corresponds to  $-\log(\text{H}^+) = 9.96$ , while the interpolated value on the curve at  $C = 0.0001$  is 10.1. This point is difficult to realise experimentally. Two determinations were made by the electrometric method of the hydron concentration of water saturated with Iceland spar and decinormal with respect to NaCl or KCl.

First result     $\langle H^* \rangle = 9.3 \times 10^{-11}$ .      Second result     $\langle H^* \rangle = 4 \times 10^{-10}$ .  
                    $-\log \langle H^* \rangle = 10.03$ .                                 $-\log \langle H^* \rangle = 9.40$ .

The saturation was effected by a current of air free from  $\text{CO}_2$  in the first case, by shaking in a silver bottle in the second case.

The experiments were made in the Muspratt Laboratory, Liverpool; the second in conjunction with Mr. J. Twomey.

The alkalinity of filtered  $\text{CaCO}_3$  solution (without chloride) was also measured by the colorimetric method (using phenolphthalein), both in deep Nessler glasses and in a Donnan colorimeter. The comparison solution was an alkaline phosphate of which  $(\text{H}^+) = 7.1 \times 10^{-10}$ . The mean of five measurements gave for the carbonate solution  $(\text{H}^+) = 4.3 \times 10^{-10}$ .

An unsteadiness in the results is to be expected, both on account of the slowness of the heterogeneous equilibrium, and on account of the extreme sensitiveness of the alkalinity to traces of  $\text{H}_2\text{CO}_3$  in this part of the curve, which is accentuated by the high dilution. A discrepancy between the observed and calculated alkalinities of sodium acetate has been accounted for by Walpole on similar grounds.§

The acid part of the curve may be tested by the help of the measurements of Walker and Kay.|| Waters of different "degrees of hardness" made from standard lime-water were brought into equilibrium with the  $\text{CO}_2$  of the air, and the acidities were measured by a colorimetric method :—

Concentration of carbonate expressed as molecules $\text{CaCO}_3$ .	$(\text{H}^+)$ .
0.035	$1 \times 10^{-8}$
0.045	$1.1 \times 10^{-7}$

\* 'Zeitsch. f. phys. Chem.,' vols. 12, 44, 64 (1893-1903).

† 'J. Amer. Chem. Soc.,' vol. 33, p. 468 (1911).

† 'Phil. Mag.,' I, p. 958 (1912).

§ 'Trans. Chem. Soc.,' vol. 105, pp. 2502, 2511 (1914).

|| 'J. Soc. Chem. Ind.,' vol. 31, p. 1014 (1912).

These figures suffice for a calculation of the degree of neutralisation  $R$ , for the total alkali (in equivalents) is 0.001 and 0.0001, and the same figure represents the bicarbonate ion concentration ( $\text{HCO}_3'$ ), since it can be shown that the fraction of original  $\text{HCO}_3'$  forming  $\text{H}_2\text{CO}_3$  is negligible at the hydron and total concentrations given. The excess of carbonic acid,  $\text{H}_2\text{CO}_3$ , should be that which is in equilibrium with the  $\text{CO}_2$  pressure of the air, *i.e.* by Bohr and Boek's results  $1.35 \times 10^{-5}$ .

It may, however, be derived with more certainty from the constant of the homogeneous equilibrium

$$(\text{H}_2\text{CO}_3) = \frac{(\text{H}') \times (\text{HCO}_3')}{K_1}.$$

This gives in the first case

$$(\text{H}_2\text{CO}_3) = 3.29 \times 10^{-5},$$

and in the second case

$$(\text{H}_2\text{CO}_3) = 3.63 \times 10^{-5}.$$

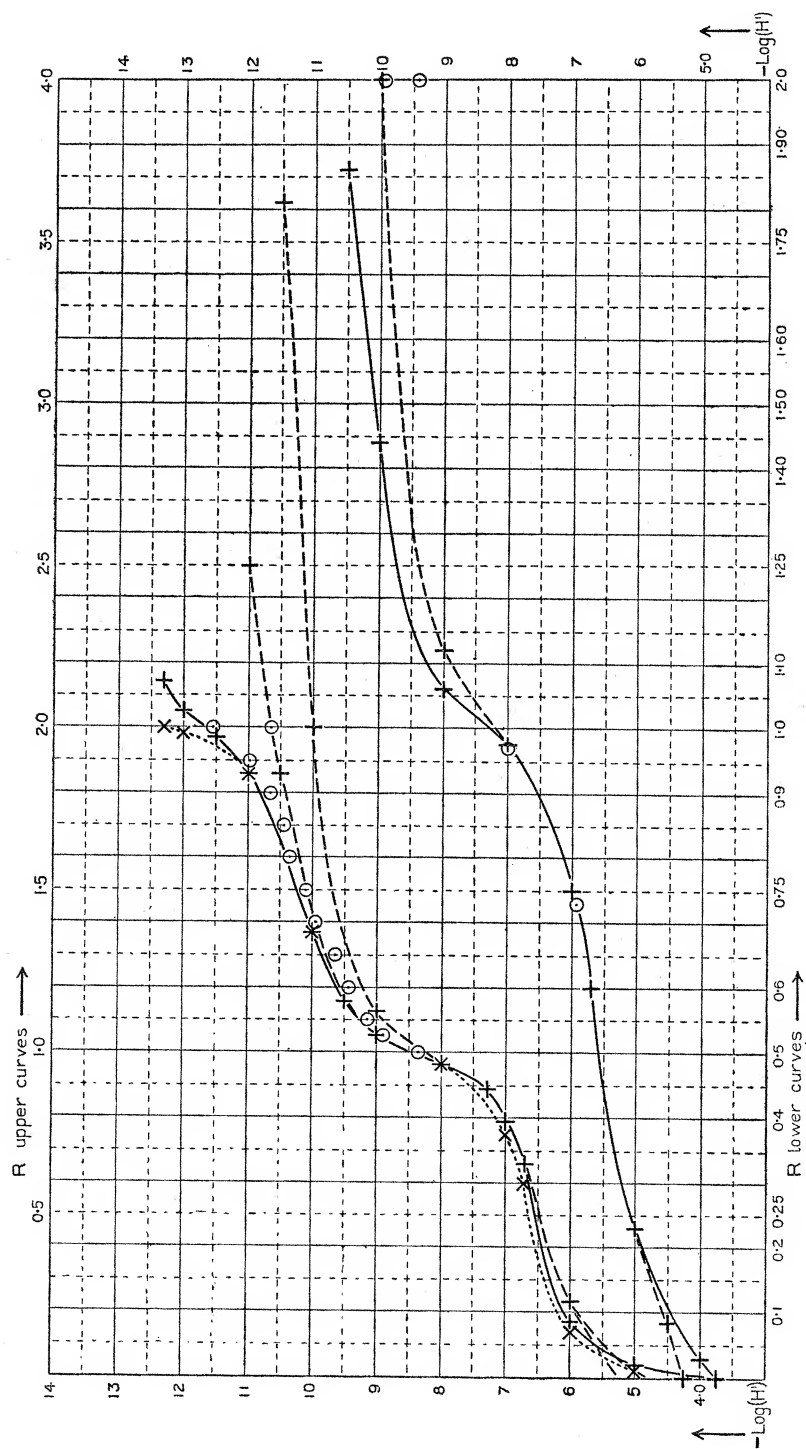
Introducing these values, the ratio  $R$  is found to be in the first case 0.97, and in the second case 0.73.

The values of the ratio from the general equation at the given acidities  $C = 0.001$  and  $C = 0.0001$ , are 0.98 and 0.75 respectively.

If, however  $(\text{H}_2\text{CO}_3)$  is calculated from the absorption coefficient of the gas-liquid equilibrium as above, the calculated value of  $R$  in the second case falls right off the curve.

The observation that  $(\text{H}_2\text{CO}_3)$  calculated from the homogeneous is slightly greater than that calculated from the heterogeneous equilibrium has been made by several investigators and has not yet been adequately explained.

It is clear from all the evidence that has come under the author's view that the data of the heterogeneous equilibria, *i.e.* pressure of  $\text{CO}_2$  and solubility of  $\text{CaCO}_3$ , can only be used with great caution to calculate  $(\text{H}')$  by means of the  $(\text{H}_2\text{CO}_3)$  and  $(\text{CaCO}_3)$  (solubility product) which are supposed to be in equilibrium with the gas and solid phase respectively. On the other hand, the analytical data, total concentration of  $\text{H}_2\text{CO}_3$  and of alkali in a homogeneous solution, can be so used with considerable confidence. The easiest method of employing the equations is evidently to plot a section of the curve corresponding to the known carbonic acid concentration, choosing values of  $(\text{H}')$  above and below that which is to be expected. The ordinate from the value of  $R$  found then gives the correct figure.



Theoretical and Experimental Neutralisation Curves of Carbonic Acid at Different Concentrations.



NOTES ON DIAGRAM.

*Ordinates* =  $-\log (H')$ . Left-hand numbers refer to upper curves, right-hand to lower.  
*Abscissæ* = ratio alkali to acid. Upper numbers refer to upper curves, lower numbers to lower curves.

*Upper Curves.*

++ and plain line—values calculated by formulæ 3a and 3b	} at C = 0·1.
× × and dotted line—values calculated by formula 1	
⊙ ⊙ Auerbach's values	at C = 0·2.
++ and broken line—values calculated by formulæ 4a and 4b	{ at C = 0·001 upper. at C = 0·0001 lower.

*Lower Curves*—Dilute carbonate on larger scale.

++ and plain line—values at C = 0·001.  
 ++ and broken line—values at C = 0·0001.  
 ⊙ ⊙ experimental values as quoted.

N.B.—The third points in Tables I and II have been erroneously plotted as 0·17 and 0·14.

*Volatilisation of Extremely Thin Radioactive Deposits.*

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(Communicated by Prof. Sir E. Rutherford, F.R.S. Received July 1, 1915.)

*Introduction.*

Within the last few years papers dealing with the volatilisation of radioactive substances have been published by various authors. The principal aims of the experiments described in these papers may be classified under three heads:—

- (a) To determine the temperatures of volatilisation of the various members of the active deposits of radium, thorium, and actinium; in some cases with a view to the classification of these substances in the periodic system.
- (b) To prove that these extremely small quantities of matter form definite chemical compounds in a manner similar to that of the commoner elements.
- (c) To separate the various members of the series from one another.

Other interesting results, which throw light on the phenomena of volatilisation, have also been reported, but these have always formed a subsidiary part of the researches described. Makower\* determined the

\* Makower, 'Manch. Lit. and Phil. Soc.,' vol. 53, Part II (1909), and 'Le Radium,' vol. 6, p. 50 (1909).